

Investigations on the plasma-surface interaction during DBD-treatment for low-temperature direct silicon wafer bonding

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Abstract:

Modification of native oxide layers on Si by dielectric barrier discharge (DBD) treatment in O₂ is an innovative activation method for low-temperature direct Si wafer bonding. Plasma-treated SiO₂ layers are analyzed by spectroscopic methods (FTIR, XPS, ellipsometry), XRR, AFM and contact angle measurements. Reasons for improved low-temperature (100 °C ≤ T ≤ 200 °C) bond strengthening after DBD activation are discussed.

Keywords: DBD treatment, low temperature direct bonding, silicon oxide, surface activation

1. Introduction

Direct wafer bonding is a widely used encapsulation technology for micro-electromechanical systems (MEMS). DBD-treatment prior to bonding can be extremely helpful in order to reduce the thermal budget, required to achieve strong bonding of the processed wafer and the cap wafer. While the benefit of the DBD-treatment in terms of tensile strength should become clear immediately from Fig. 1, the physical and/or chemical reasons leading to this effect are still under investigation. Various effects, which are induced by DBD-treatment to the topmost nanometers of the covering native silicon oxide, can principally be taken into account to be responsible.

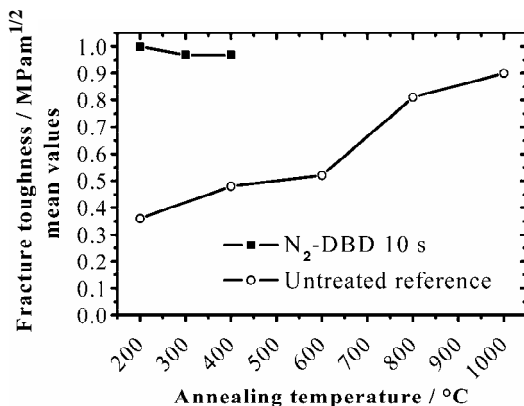


Fig. 1: Comparison of fracture toughness versus annealing temperature with and without DBD-activation, resp. (from [1])

Separating the importance of the individual effects is motivated by the challenge of further optimizing the activation process and also by the selection and development of new activation processes.

2. Experimental

The wafer material for transmission infrared spectroscopic investigations was double side polished, n-doped [100]-oriented float-zone silicon with a resistivity of 3-5 Ωcm and 4" diameter. For direct bonding experiments, we used single side polished, p-doped CZ-grown prime grade [100] silicon wafers with 100 mm diameter. The thickness of all wafers was 525 μm with a total thickness variation of ±25 μm.

Wet chemical surface cleaning prior to DBD treatment was done by immersion of the wafers into SC1 (H₂O₂ : NH₃ : DI-H₂O with a mixing ratio of 1:1:5) and SC2 (H₂O₂ : HCl : DI-H₂O with a mixing ratio of 1:1:6), both heated to 75-80 °C, for 10 min with a subsequent DI-water rinse for the same time.

For the DBD treatment, the samples were fixed on an electrically grounded vacuum chuck, while the oxygen process gas flowed through a 300 μm gap above it. The counter electrode was formed by a layer of indium-doped tin oxide (ITO), sputtered on a 0.7 mm thick glass substrate, serving as the dielectric barrier. A high voltage was applied to the top electrode in order to ignite the discharge in the gap.

Infrared spectra were taken with a Thermo Nicolet 5700 FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector. The ν_{as}(Si-O) vibration was analyzed from single transmission measurements with parallel polarization under 74° incidence and a resolution of 4 cm⁻¹.

XPS analysis was done with a PHI 5500 Multi-Technique system from Perkin-Elmer equipped with a Mg Kα X-ray source (1253.6 eV) without a monochromator in a vacuum better than 8·10⁻⁹ mbar during the measurement. The collection angle was 34°, the X-ray spot size 400 x 400 μm².

For optical characterization in the visible regime, a Sentech SE800 (Sentech Instruments GmbH, Germany)

variable-angle spectroscopic ellipsometer was used. All samples were measured at four different angles (58°, 62°, 66°, and 70°) with additional use of a retarder. A three-layer stack was used for the fit procedure with the Jellison model for [100]-oriented silicon [43] at the bottom, followed by a layer with constant refractive index representing the DBD-modified silicon oxide, and air as top layer.

AFM measurements have been done in tapping mode with a silicon tip, covered by native oxide, using a Veeco DI3100. Scan ranges of 1.1 μm^2 were chosen for rms roughness (R_q) calculations.

3. Results and discussion

3.1. Roughness

Among all bonding techniques (i.e. glass frit bonding, eutectic bonding etc.), direct bonding requires the lowest surface roughness. According to literature, R_q values below 0.5 nm are favorable in order to achieve spontaneous bonding [2].

We measured surface roughness for various DBD treatment times by AFM. R_q for the RCA-cleaned reference was 0.18 ± 0.04 nm. No significant increase or decrease of surface roughness was found neither in the normal O_2 -DBD treatment time range between 30 s to 40 s nor in a series of experiments with shorter and longer treatment time ranging from 5 s to 400 s.

For DBDs at atmospheric pressure, the hazard of surface roughening due to impinging ions is very small, because the ion energy in the DBD will hardly exceed a few tens of eV.

3.2. Hydrocarbon removal

Due to the generation of oxygen radicals and ozone in the discharge, atmospheric pressure plasma can effect surface cleaning, i.e. the removal of organic contaminations.

We compared a multitude of C1s XPS spectra from measurements on silicon samples in their original state as delivered from the manufacturer, after RCA-cleaning and after O_2 -DBD, respectively.

However, we did not figure out a significant difference among the spectra for the various surface treatments. We therefore assume, that the contamination level is already at a very low level, therefore the surface cleaning capabilities of the DBD seems to be of minor importance.

3.3. Oxide buildup

Starting from a native oxide layer of 0.7 nm thickness after RCA-cleaning, we investigated the increase of film thickness over treatment time, ranging from 1.5 s to 350 s. FTIR and XPS spectra as well as XRR and ellipsometric measurements lead to the coincident picture of a growing oxide film with the time dependence as shown in Fig. 2.

Within only a few minutes treatment time the oxide thickness grows considerably by several nanometers. The

fit curve shows a logarithmic dependence. According to Collot [3], this type of growth law can be explained by an exponentially declining flux of oxidizing species with increasing film thickness.

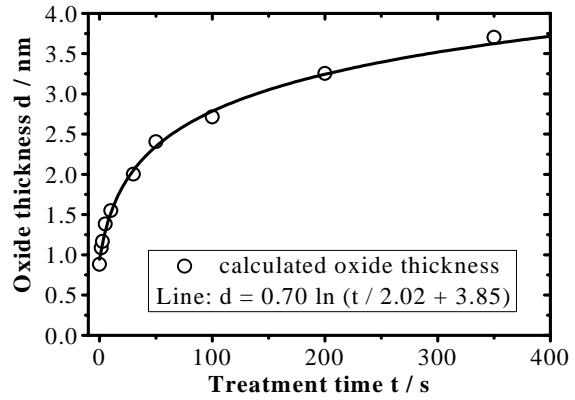


Fig. 2: Oxide thickness as calculated from XPS measurements and logarithmic fit curve.

3.4. Oxide structure

Apart from the mere effect of oxide growth, special attention should also be paid to the physical and chemical properties of the DBD-treated oxide film. The oxide which is present on the silicon surface prior to DBD-treatment is also subject to modification. This can be concluded from the $\nu_{\text{as}}(\text{Si-O})$ absorption in the infrared spectrum of a thin thermal oxide, which was reduced through DBD treatment, i.e. silicon-oxide bonds were broken and substituents (e.g. OH or H) were attached to these sites.

A number of further indicators were found, leading to the consideration that the density of the DBD-modified oxide film is reduced as will be outlined below.

3.4.1. LO and TO band positions

In Fig. 3 the $\nu_{\text{as}}(\text{Si-O})$ vibration spectra are shown for thermal oxide and a native oxide, treated 10 s with O_2 -DBD.

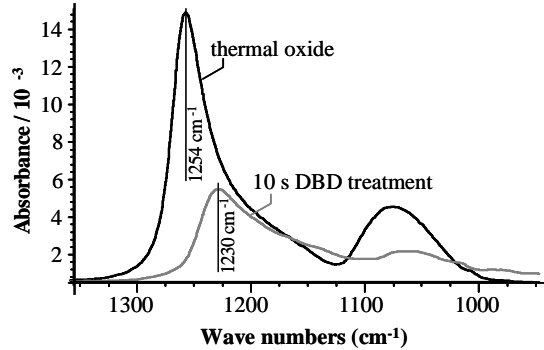


Fig. 3: Infrared spectra of thermal oxide and native oxide after 10 s DBD treatment.

A difference of 15 cm^{-1} can be found for the position of the TO bands, located at 1060 cm^{-1} for the DBD-modified oxide and 1075 cm^{-1} for thermal oxide, respectively. The LO peaks are separated even by 24 cm^{-1} . While the LO peak related to thermal oxide is located at 1254 cm^{-1} , which is in good agreement with literature values [4] [5], that of oxide grown under influence of O_2 -DBD can be found at 1230 cm^{-1} .

The dependence of the LO and TO absorption band position on several influences through film composition has been discussed very thoroughly by Queeney et al. [5]. In a recent publication, we already discussed in detail that the observed shift of the LO mode for DBD-modified oxide can be attributed to the formation of pores in the oxide with a pore volume of approximately 10 vol% [6].

3.4.2. XPS attenuation length

The attenuation length λ of Si2p photoelectrons in an oxide, grown within 30 s under O_2 -DBD influence, could be calculated thanks to the precise knowledge of the film thickness from independent XRR measurements.

Our result for λ ($\lambda_{\text{SiO}_2} = 3.112 \text{ nm}$) is about 4 % larger than the literature value for thermal oxide ($\lambda_{\text{SiO}_2} = 2.996 \text{ nm}$, [7]), showing the same tendency as the estimation of pore fraction from the infrared measurements.

3.4.3. Refraction index

A further indication for the inclusion of pores in the DBD-modified oxide can be found in the ellipsometric data. The spectrum of the DBD-modified oxide film can be fitted very well with a Bruggemann EMA model, where the fraction of vacuum pores ($n = 1$) within a silicon oxide matrix ($n = 1.4534$) is fitted.

The result yields a pore fraction of roughly 6 % for 2.0 nm thick oxide grown within 30 s under O_2 -DBD influence, leading to the same refractive index ($n=1.430$) as if fitted with a model of constant refractive index.

3.4.4. Etch profile

The oxide film thickness of RCA-cleaned references as well as additionally O_2 -DBD treated samples were measured by means of ellipsometry after immersion in 0.05 % HF for 10 s up to 150 s. Resulting etch profiles are shown in Fig. 4.

Apart from the obvious difference in initial oxide film thickness, a largely increased etch rate especially near the oxide surface characterizes the DBD-modified samples.

Assuming that the etch rate of the oxide film is related to its density, the latter should consequently be lowest directly at the surface while gradually increasing with further distance from the former increasing depth.

The curves for the investigated treatment time between 10 s and 350 s in O_2 -DBD are all of congruent shape.

Interestingly, this particular etching curve shape, where the etch rate gradually decreases over 150 s etching time,

seems to be a necessary condition leading to high bond energies. Removing more than about 2/3 of this layer results in drastically reduced bond energy.

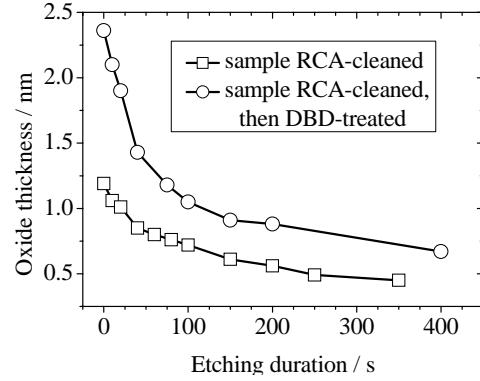


Fig. 4: Oxide thickness over etching time in diluted HF.

3.5. Long term reaction

Another characteristic for O_2 -DBD treated samples can be found in long term changes of the $\nu_{\text{as}}(\text{Si-O})$ band in the infrared spectrum. Over a 48 hours period of storage in air, significant change of the LO mode absorption band height as well as a slight shift to higher wave numbers can be observed. The magnitude of these long term reactions depends on treatment time.

Fig. 5 shows the LO mode absorption band height measured from top to baseline over storage time.

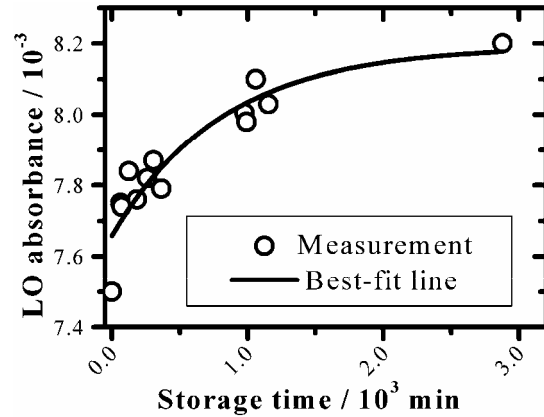
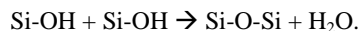


Fig. 5: LO peak height plotted against storage time.

Numerous reasons (e.g. a collapse of pores, condensation of silanol groups, relaxation of strained bonds, oxidation process at the Si/SiO₂ interface etc.) could serve as an explanation for this behaviour. Further experiments, designed to deliver a detailed picture of the mechanisms, are still in progress.

3.6. Silanol group density

The existence of silanol groups at the mating surfaces is a commonly accepted prerequisite for successful hydrophilic direct wafer bonding. Models to explain the mechanisms of bond strengthening always incorporate the condensation reaction of silanol groups into siloxane bonds:



It therefore seems quite reasonable to investigate in how far the improved bond strength of DBD-activated surfaces is a result of increased bonding sites. In order to approach this question, three different techniques were applied:

3.6.1. Infrared SiO-H absorption band

The presence of silanol groups can be principally verified by means of infrared spectroscopy. Unfortunately, in the range of interest between 3000 cm^{-1} and 4000 cm^{-1} a multitude of O-H related absorption bands are located.

Especially the broad and featureless absorption band of incorporated molecular water, which stretches out over the whole wavenumber range, covers the less pronounced SiO-H absorption band.

At the present state of our investigations, no analysis of the silanol group density can therefore be given, yet. However, a significant amount of water seems to be introduced and distributed in the oxide film by DBD-treatment.

3.6.2. Contact angle measurements

Water contact angle measurements offer a simple and surface sensitive measure of the hydrophobicity or hydrophilicity of a surface. Since the surface hydrophilicity state of RCA-cleaned and DBD treated samples already leads to water contact angles as small as $3\text{--}5^\circ$ in air, the Schultz method, where hexadecane is involved as third phase, was applied.

The Schultz method reveals a slight difference of contact angles: the mean value for RCA-cleaned samples was $23.1^\circ \pm 1.9^\circ$, whereas a mean value of $17.1^\circ \pm 1.5^\circ$ after O_2 -DBD treatment was determined.

The results indicate an increase of silanol density through O_2 -DBD treatment within a range of 20 to 30 % which is, however, far away from serving as an explanation for the dramatic increase of bond energy as shown in Fig. 1. A more precise relation between the contact angle and silanol density has not been determined, yet.

3.6.3. Chemical derivatization

Another approach to silanol density analysis was made with a derivatization method using a fluorinated monomethoxy silane. Preliminary experiments are in good agreement with the results from contact angle measurements, showing a normalized F1s/Si^{2p} peak area ratio of 0.30 for RCA-cleaned wafers and 0.42 for O_2 -DBD

treated samples, respectively.

Presumed that all of the OH groups at the surface could react with the derivatization reagent (i.e. steric hindrance did not prevent completion of the derivatization reaction), this would mean a relative increase of 30 % through DBD-treatment.

Efforts for the conversion of the normalized F1s/Si^{2p} peak area ratio into a quantitative silanol density are currently being made.

4. Conclusions

The species in a dielectric barrier discharge (DBD) in oxygen process gas lead to a multitude of effects on the surface of a native oxide covering a silicon wafer.

The plasma process can be described as an activation, inasmuch that hydrocarbon contaminations are removed from the surface as well as silicon oxide bonds are broken and replaced by -OH groups, which leads to improved surface wettability.

Although sputtering does not occur due to the small ion energy, thanks to the atmospheric pressure of the process gas, the density of the oxide structure is greatly affected during O_2 -DBD treatment.

Two positive effects for successful low temperature direct wafer bonding can be deduced from the results presented above: First, surface roughness is virtually unchanged through the activation procedure, while - secondly - a porous oxide of increasing thickness is formed. Thanks to the porosity of the oxide, water molecules, trapped at the pre-bond interface and additionally liberated in the silanol condensation reaction (see 3.6.) can soak into the oxide more easily upon annealing.

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